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TITLE

Application of Ultraviolet Spectroscopy for Monitoring Oil in Water

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Application of Ultraviolet Spectroscopy for Monitoring Oil in Water

by Clive MacGregor
Seatech Ltd.
and
Dwight Veinot
Defence Research Establishment Atlantic, Dockyard Laboratory (Atlantic)
Dartmouth, Nova Scotia, Canada B2Y 3Z7

ABSTRACT

This paper will discuss the usefulness of ultraviolet spectroscopy for determination of low levels of oil in water. The presentation will include the findings of a laboratory study and relate this work to the use of ultraviolet spectroscopy in the detection of oil in water from oil rig discharges, tanker discharges and oil spills at sea.

The test program was essentially a matrix test where different types of oil (diesel, naval distillate, lubricating oil and hydraulic oil) were mixed at concentrations from 0 to 100 ppm and detected using various wavelengths for ultraviolet absorbance and ultraviolet fluorescence. Limits of detection, linearity, interference, and phase effects (ie. dissolved versus particulate oil) were assessed.

The results indicated that both ultraviolet absorbance and fluorescence could detect oil in water at 1 ppm, though experience indicated that fluorescence was about one order of magnitude more sensitive. The linearity of response was acceptable for both detection methods over the range 0 to 25 ppm. Beyond this range both methods tended to significantly under report the oil present. Interference from bilge cleaners, solids and other chemicals were very pronounced for ultraviolet absorbance, but were almost non existent for ultraviolet fluorescence. These interference results were consistent with previous site experiences testing Oil Detection Monitors on various oil tankers and in other similar applications.

The major problem with all Oil Detection Monitors with regard to calibration was reconfirmed for these detection formats. The response of the detector varies depending on the type of oil present. Thus the calibration of a unit to produce accurate readout of part per million oil in water is very problematic. Experience in the field with existing oil tanker or rig discharges show that where a variety of oils may be present the Oil Detection Monitors are often inaccurate, and generally under report significantly. Thus a simple colorimetric detector tube which could measure total oil in water at part per million levels would be a useful addition to any onboard monitoring equipment. This presentation will conclude with some preliminary results on the development of such a device.

METHODS FOR DIRECT CONTINUOUS MONITORING OF OIL IN DISCHARGED WATERS

1) WHITE LIGHT SCATTERING

-based on scattering by oil droplets of a light beam, measure back scatter or loss of light transmittance.
Advantages: robust, rugged & inexpensive.
Disadvantages: not specific to oil, does not detect dissolved oil, interference from solids in discharge, high error at 15 ppm oil in water.

2) INFRA RED DETECTION

-based on infrared light absorption by C-H bond vibration, thus less IR light transmittance more oil in the water.
Advantages: specific to organics, detects dissolved oil in water
Disadvantages: will detect other organics as oil (eg sewage), some interference from solids but less than white light, limit of detection is approx. 5 ppm or worse, more technically demanding to operate.

3) ULTRAVIOLET DETECTION

-based on either absorption of UV light exciting conjugated double bonds (ie aromatic fraction), or absorbance and fluorescence in the UV from excited conjugated double bonds.
Advantages: more specific to oil, detects dissolved oil in water, low level of detection to 1 ppm or less.
Disadvantages: more expensive and technically demanding to operate, UV absorption affected by additives (eg soaps)

LEGISLATIVE REGIME

International Maritime Organization (IMO) and Canada Shipping Act

Effective July, 1998 new oil in water discharge levels from vessels in coastal waters regulated.
-applies to all oil tankers over 150 GRT & all vessels over 400 GRT
-there are four allowed levels:
- 5 ppmv in Inland waters
- 15 ppmv in specified coastal waters
- 100 ppmv 12 nautical miles
- 30L/nm 50 nautical miles

-there are two levels of monitors specified, those for 15 ppmv and 5 ppmv (some vessels allowed 15 ppmv discharge will need 5 ppmv monitors)
-the regulation specifies control systems, separation and filtration equipment for any ship discharges.
-specifies records be kept of discharges, maintenance and calibration, and annual steamship inspector inspections.

What determines exceedance of this criteria?

Sample collected and analyzed in a lab, or a visible sheen coming from the suspect vessel with concurrent oil identification (comparison of oil on water sample with samples from suspect vessel). To varying degrees the results from the oil detection monitor will be accepted as proof of compliance (obviously good records of calibration and maintenance, or some independent test would be useful).

OBJECTIVE

Determine the generic capability of Ultraviolet spectroscopy to detect oil in Canadian Naval vessel discharges at levels of 1 ppmv.

White light scattering and Infra Red were eliminated from consideration due to lack of ability to readily detect dissolved oil, the effect of interferences, and insufficiently low level of detection.

A review of the literature indicated that several UV Fluorescence detector systems existed, but there were few scientific evaluations (not including the manufacturer). Several other types of commercial detectors using technologies noted above also existed.

The assessment was designed to test response from lab UV spectrometers for both UV absorption and UV fluorescence. The tests were undertaken on five oils:

- Diesel Fuel
- Naval Distillate
- Diesel Motor Oil
- Synthetic Lube Oil
- Hydraulic Fluid

Over the range 0 to 100 mg/L.

Note: 0.7 mg/L = 1 ppmv.

UV SPECTRAL ANALYSIS OF THE OILS IN WATER

1) Is there a single wavelength which might be on average be appropriate to use for reliable detection of oil in discharged water ?

2) What was the variation of response with oil type and might there be an average oil mixture to use ?

3) What amount of oil was dissolved in the water, as this is much harder to remove than oil droplets (particulate oil) ?

4) What factors cause interferences in the detection of oil in water ? (Not a topic of this study but reviewed outside this work).

5) What is a reasonable limit of detection based on these laboratory tests and is there linear response around 20 ppmv ?

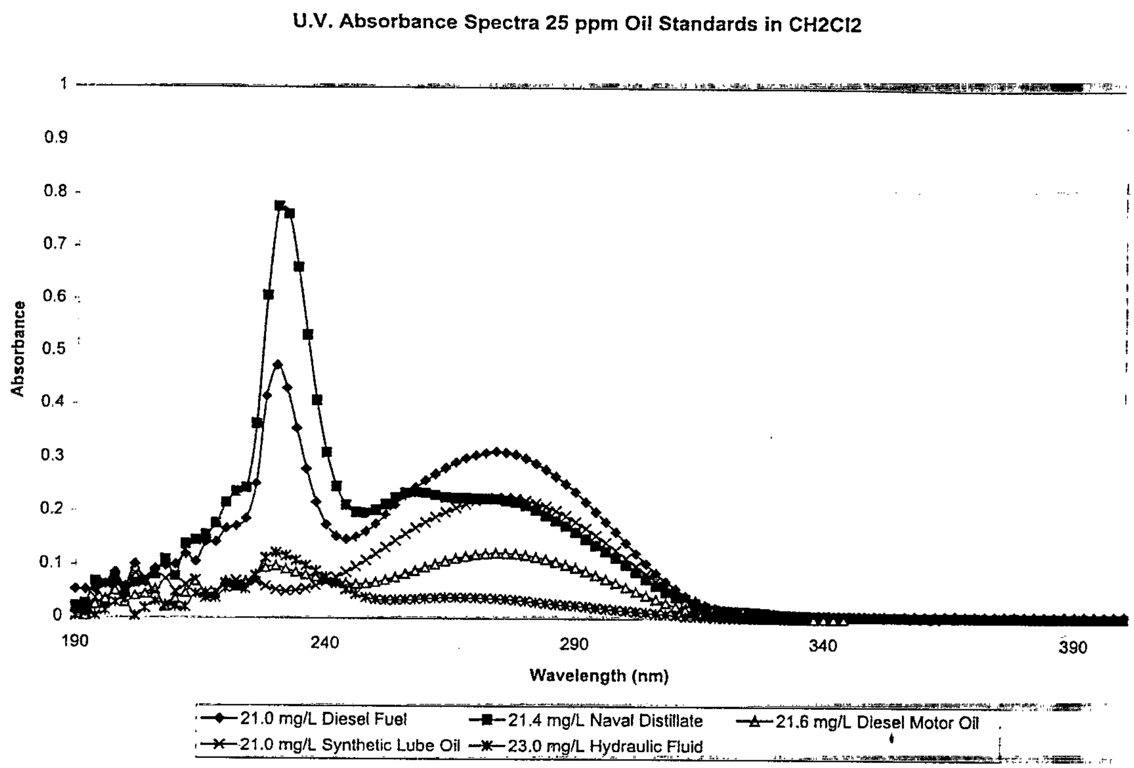

Figure 3.2.1

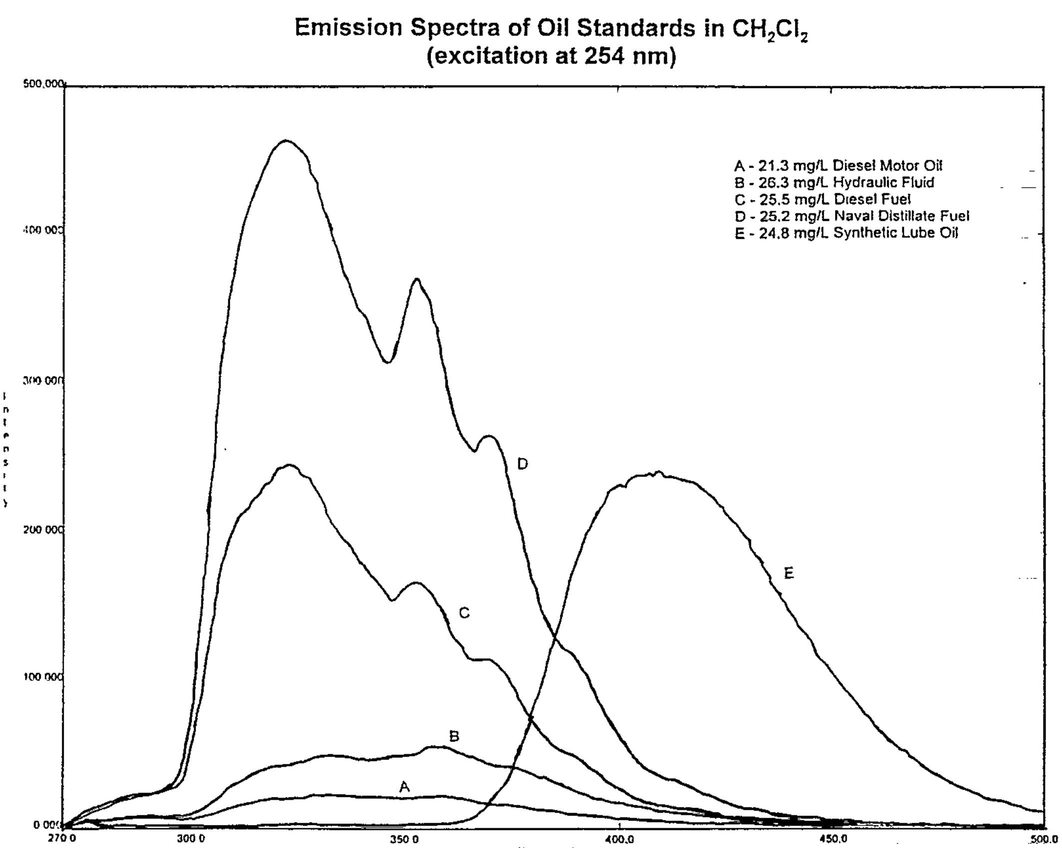

Figure 3.2.2

PERCENT DISSOLVED OIL FOR

OIL AT APPROXIMATELY 20 MG/L

OIL TYPE	PERCENT DISSOLVED
Diesel Fuel	75-80
Diesel Motor Oil	5-15
Hydraulic Fluid	15-60
Naval Distllate	10-70
Synthetic Lube	30-80

Variability caused by effect of different agitation times, and potentially some wall effects.

INTERFERENCES ON UV OIL DETECTION
(Based on literature and other knowledge)

UV ABSORBANCE

-soaps (degreasers) could cause up to 100%+ positive error in determination of oil in discharge water.
-solids (eg rust) caused some positive reading effects.

UV FLUORESCENCE

-soaps and chemicals had little effect on the determination of oil in discharge water.
-solids had very little effect on readings.

LIMIT OF DETECTION AND LINEARITY

Limits of detection were calculated using a twice baseline noise response criteria at 1 to 10 ppmv.

UV ABSORPTION	1.4 mg/L	+-0.7 mg/L
UV FLUORESCENCE	0.3 mg/L	+-0.13 mg/L

Note this is laboratory best case, and may not represent field capability

Linearity can best be descibed by a least squares regression calculation R^2 (over the range 0 - 100 mg/L).Better linearity is described by

UV ABSORPTION	0.58	(Hydraulic was 0.01)
UV FLUORESCENCE	0.94	

CONCLUSIONS

1) To ensure there is no discharge above limits there is no simple electronic detection system that will reliably determine mixtures of oil in discharge water.

This fact is not due to lack of capabilities of the detectors but rather the variability of the potential discharge mixtures (ie lubes in with Naval Distillate,etc).

A unit calibrated on Naval Distillate at that wavelength will under report Lubricating oil by over a factor of ten.

These systems work very well in situations where the oil is of one type such as for a production platform on a specific field (eg the Cohasset field off Sable Island).

2) UV Fluorescence is the preferred method for oil detection and is presently in use at many locations, but some of the units used in oil fields offshore may be inappropriate for vessels with a lot of movement. This is because the units use "falling stream detection" to prevent fouling of detector windows. Some other changes to UV Fluorescence specific to the offshore oil production may not be needed or may be counter productive for shipboard use (eg size, falling stream, etc).

3) Electronic units always carry a higher cost of maintenance and calibration and the need for independent checks on performance (lab samples or other test methods).